学校编码：10384　　分类号_____密级_____

学　　号：20620101151424　　UDC_____

厦门大学

硕　士　学　位　论　文

# 一氧化碳低温氧化负载型钯催化剂的侧柏叶浸出液辅助还原制备与性能研究

# Study on Supported Pd Catalysts Biosynthesized by *Cacumen Platycladi* Extract and their Catalytic Performance on Low Temperature Oxidation of CO

国家自然科学基金重点项目(21036004)资助

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论文提交日期：　2013年　月

论文答辩日期：　2013年　月

学位授予日期：　2013年　月

答辩委员会主席：_____

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2013年　月

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# 摘 要

CO 低温氧化反应在汽车尾气处理、封闭式-循环 $CO_2$ 激光器、氢燃料电池中少量 CO 的消除及作为催化领域模型反应等方面都有重要应用。近年来，研究者致力于改进催化剂的制备方法，以期获得低温下高活性、高稳定性的催化剂。本论文将植物还原法引入 Pd 催化剂的制备过程，分别采用溶胶负载法（SI 法）和吸附还原法（AR 法）制备负载型 Pd 催化剂，将所制备的 Pd 催化剂进行表征，并用于 CO 低温氧化体系中，考察催化剂制备条件对反应性能的影响，优化催化剂的制备条件，探索催化剂的结构和表面性质与催化反应性能之间的关系。

首先采用 SI 法制备了 Pd 催化剂，研究结果表明：通过改变反应温度、侧柏叶浸出液浓度及 Pd 前驱体的浓度可以调节 Pd 纳米颗粒的粒径，Pd 颗粒粒径越小催化活性越高。侧柏叶浸出液浓度过高，虽然会获得粒径较小的 Pd 纳米颗粒，但同时也覆盖了 Pd 催化剂的活性位点，导致催化剂活性降低。经过焙烧处理去除催化剂表面的生物质，催化剂活性提高，此时催化剂表面为 $Pd^{2+}$物种，说明氧化态的 $Pd^{2+}$可作为该反应的活性物种。经过氢气还原处理后，催化剂表面部分 $Pd^{2+}$被还原为 $Pd^0$，导致催化活性再次提升，表明 $Pd^0$ 物种也是 CO 氧化体系中催化剂表面的活性物种。催化剂活性数据结果表明：溶胶负载法制备，以 $Pd(NO_3)_2$ 为前驱体，$CeO_2$ 为载体，Pd 理论负载量为 0.5 wt.%，侧柏叶浸出液浓度为 5 g/L，空气气氛下 300 $^oC$ 焙烧 2 h，氢气中 500 $^oC$ 还原处理 2 h 制得的 Pd 催化剂活性较优。在空速 6000 $mL/g_{cat}/h$，原料气比例 $CO/O_2/N_2$ = 1/1/98，反应温度 30 $^oC$ 时 CO 转化率为 49.6 %，50 $^oC$ 时 CO 转化率可达到 100 %。

采用 AR 法制备了 Pd 催化剂，实验结果表明：以不含 $Cl^-$离子的 $Pd(NO_3)_2$ 为前驱体可以获得较高的催化活性，以 $CeO_2$ 为载体，以侧柏叶浸出液做还原剂制备所得的催化剂活性较优。该法不但可以有效地将 Pd 负载于 $CeO_2$ 载体上，而且在高负载情况下亦可以实现 Pd 的高分散。和 SI 法所获催化剂类似，在空气氛围中一定温度下焙烧催化剂可以除去催化剂表面残留的生物质，暴露出催化剂的活性位点从而提高催化剂的活性，同样经过焙烧之后的催化剂表面 Pd 物种被氧化为 $Pd^{2+}$，此时的 $Pd^{2+}$不是以 PdO 形式而是以 $Pd_xCeO_{2-\delta}$ 固溶体的形式存在。对 AR 法制备的 $Pd/CeO_2$ 进行氢气还原处理，还原后催化剂活性有了极大的提高。对催化剂进行稳定性评价，发现催化剂活性下降后，再次通氢处理可以恢复催化

剂的活性，并且可以延长催化剂的寿命。这可能是因为反应过程中 $Pd^0$ 被氧化，而通氢处理可以使 Pd 物种恢复到金属态 $Pd^0$，并加深了催化剂表面 Pd 的还原程度。另外本文还初步探索了 $CeO_2$ 形貌对催化剂活性的影响，发现合成的纳米棒状和纳米方块状 $CeO_2$ 负载 Pd 之后都可以获得比常规 $CeO_2$ 载体更高的活性。催化剂活性数据显示：吸附还原法制备，以 $Pd(NO_3)_2$ 为前驱体，纳米棒状 $CeO_2$ 为载体，Pd 理论负载量为 0.5 wt.%，侧柏叶浸出液浓度为 5 g/L，空气气氛下 300 $^oC$ 焙烧 2 h，氢气中 300 $^oC$ 还原处理 2 h 制得的 Pd 催化剂活性较优。在空速 6000 $mL/g_{cat}/h$，原料气比例 $CO/O_2/N_2$ = 1/1/98，反应温度 30 $^oC$ 时 CO 转化率达 62 %，50 $^oC$ 时 CO 转化率可达 100 %。

**关键字：** 负载型 Pd 催化剂；CO 低温氧化；生物还原；二氧化铈

# Abstract

The catalytic oxidation of CO at low temperature has attracted considerable attention because of its wide applications in automotive emission control, exhaust abatement for $CO_2$ lasers, CO preferential oxidation for proton exchange membrane fuel cells and as a prototypical reaction for heterogeneous processes. It is necessary to introduce eco-friendly and low-priced process to prepare effective catalysts with high activity and stability for CO oxidation at low temperature. In this paper, a new green method integrating bioreduction and immobilization was developed to prepare supported Pd catalysts for CO oxidation. Specifically, supported Pd catalysts were prepared by sol-immobilization method (SI) and adsorption-reduction (AR) method respectively using plant extract as reductant and stabilizing agent. The influence of catalysts preparation conditions on CO catalytic activity were investigated and the catalysts were characterized by a variety of technigques to research the relationship between structure and surface properties of catalysts and their catalytic performance.

Firstly, SI method was employed to prepare supported Pd catalysts. The results showed that the size of Pd nanoparticles (PdNPs), which had significant impact on catlytic performance, could be controlled by the adjustment of reaction temperature, concentration of *Cacumen Platycladi* (CP) extract and Pd precursor. And smaller PdNPs had a better catalytic activity in CO oxidation. However, smaller PdNPs achieved with a high CP concentration caused a low activity because the surface active sites were covered by the biomass. Calcination could remove the biomass residual and expose the active size on supported Pd catalysts, accordingly the catalytic activity of catalysts increased after calcination. The Pd species on the catalysts surface were in $Pd^{2+}$ state, which showed that $Pd^{2+}$ could act in CO oxidation. It was also found that $H_2$ could remarkably improved the conversion of CO oxidation at low temperature. After $H_2$ reduction, $Pd^{2+}$ on the catalysts surface turned to $Pd^0$, which proved the $Pd^0$ was more effective and active species than $Pd^{2+}$ in CO oxidation at low temperature. As a result, the optimum conditions of preparing $Pd/CeO_2$ catalyst was as follows: Pd loading of 0.5 wt.%, CP extract concentration of 5 g/L, calcination at 300

$^{o}$C for 2 h in air, hydrogen reduction at 500 $^{o}$C for 2 h. In this condition, CO conversion reached 49.6 % at 30 $^{o}$C and 100 % at 50 $^{o}$C under a 6000 mL/$g_{cat}$/h space velocity with $CO/O_2/N_2$ = 1/1/98.

Secondly, AR method was then used in the biosynthesis of supported Pd catalysts. The results revealed that the kinds of Pd precursors, supports, plants were highly affecting catalytic performance. It was found $Pd(NO_3)_2$ as precursor, $CeO_2$ as support and CP extract as biomass reductant could achieve high CO conversion. AR method could not only effectively load Pd on $CeO_2$, but also achieve high dispersion of Pd in the case of high Pd loading amount. Similar to SI method, calcination removed the biomass residual to expose the active sites and improved the catalytic activity. Whereas，Pd species in the catalyst prepared by AR method were existed in $Pd_xCeO_{2-\delta}$ phase instead of PdO after calcinations in air. Also, $H_2$ reduction could significantly enhance the catalytic activity by partially reduce $Pd^{2+}$ to $Pd^0$ species, which as well confirmed that $Pd^0$ was more active than $Pd^{2+}$ in CO oxidation reaction. The catalyst stability was evaluated and it was found that not only the catalyst activity could recover but also the catalyst lifetime was prolonged after $H_2$-treatment. It might be because $H_2$ reduction treatment reduced the $Pd^{2+}$ species formed in reaction process to more active $Pd^0$. Furthermore, the influence of different ceria crystal morphology on the performance of catalysts was researched and the results showed that catalysts using nanocubes and nanorods $CeO_2$ as supports exhibit higher catalytic activity than that using conventional $CeO_2$. Hence, the optimum conditions to obtain Pd catalysts by AR method was found as follows: nanorods $CeO_2$ as support, the Pd loading of 0.5 wt%, CP extract concentration of 5 g/L, calcination at 300 $^{o}$C for 2 h in air and then $H_2$ reduction at 300 $^{o}$C for 2 h. In this condition, CO conversion reached 62 % at 30 $^{o}$C and 100 % at 50 $^{o}$C under a 6000 mL/$g_{cat}$/h space velocity with $CO/O_2/N_2$ = 1/1/98.

**Keywords:** Supported Pd catalyst; Low temperature CO oxidation; Bioreduction; Ceria

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